



AFRL-OSR-VA-TR-2015-0023

(NII) - Local Electric Field Effects on Rhodium-Porphyrin and
NHC-Gold Catalysts

MATTHEW KANAN
LELAND STANFORD JUNIOR UNIV CA

01/05/2015
Final Report

DISTRIBUTION A: Distribution approved for public release.

Air Force Research Laboratory
AF Office Of Scientific Research (AFOSR)/RTE
Arlington, Virginia 22203
Air Force Materiel Command

REPORT DOCUMENTATION PAGE					Form Approved OMB No. 0704-0188	
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to the Department of Defense, Executive Service Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.</p>						
1. REPORT DATE (DD-MM-YYYY)		2. REPORT TYPE			3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE				5a. CONTRACT NUMBER		
				5b. GRANT NUMBER		
				5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S)				5d. PROJECT NUMBER		
				5e. TASK NUMBER		
				5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)					8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)					10. SPONSOR/MONITOR'S ACRONYM(S)	
					11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT						
13. SUPPLEMENTARY NOTES						
14. ABSTRACT						
15. SUBJECT TERMS						
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON	
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (Include area code)	

INSTRUCTIONS FOR COMPLETING SF 298

1. REPORT DATE. Full publication date, including day, month, if available. Must cite at least the year and be Year 2000 compliant, e.g. 30-06-1998; xx-06-1998; xx-xx-1998.

2. REPORT TYPE. State the type of report, such as final, technical, interim, memorandum, master's thesis, progress, quarterly, research, special, group study, etc.

3. DATES COVERED. Indicate the time during which the work was performed and the report was written, e.g., Jun 1997 - Jun 1998; 1-10 Jun 1996; May - Nov 1998; Nov 1998.

4. TITLE. Enter title and subtitle with volume number and part number, if applicable. On classified documents, enter the title classification in parentheses.

5a. CONTRACT NUMBER. Enter all contract numbers as they appear in the report, e.g. F33615-86-C-5169.

5b. GRANT NUMBER. Enter all grant numbers as they appear in the report, e.g. AFOSR-82-1234.

5c. PROGRAM ELEMENT NUMBER. Enter all program element numbers as they appear in the report, e.g. 61101A.

5d. PROJECT NUMBER. Enter all project numbers as they appear in the report, e.g. 1F665702D1257; ILIR.

5e. TASK NUMBER. Enter all task numbers as they appear in the report, e.g. 05; RF0330201; T4112.

5f. WORK UNIT NUMBER. Enter all work unit numbers as they appear in the report, e.g. 001; AFAPL30480105.

6. AUTHOR(S). Enter name(s) of person(s) responsible for writing the report, performing the research, or credited with the content of the report. The form of entry is the last name, first name, middle initial, and additional qualifiers separated by commas, e.g. Smith, Richard, J, Jr.

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES). Self-explanatory.

8. PERFORMING ORGANIZATION REPORT NUMBER. Enter all unique alphanumeric report numbers assigned by the performing organization, e.g. BRL-1234; AFWL-TR-85-4017-Vol-21-PT-2.

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES). Enter the name and address of the organization(s) financially responsible for and monitoring the work.

10. SPONSOR/MONITOR'S ACRONYM(S). Enter, if available, e.g. BRL, ARDEC, NADC.

11. SPONSOR/MONITOR'S REPORT NUMBER(S). Enter report number as assigned by the sponsoring/monitoring agency, if available, e.g. BRL-TR-829; -215.

12. DISTRIBUTION/AVAILABILITY STATEMENT. Use agency-mandated availability statements to indicate the public availability or distribution limitations of the report. If additional limitations/ restrictions or special markings are indicated, follow agency authorization procedures, e.g. RD/FRD, PROPIN, ITAR, etc. Include copyright information.

13. SUPPLEMENTARY NOTES. Enter information not included elsewhere such as: prepared in cooperation with; translation of; report supersedes; old edition number, etc.

14. ABSTRACT. A brief (approximately 200 words) factual summary of the most significant information.

15. SUBJECT TERMS. Key words or phrases identifying major concepts in the report.

16. SECURITY CLASSIFICATION. Enter security classification in accordance with security classification regulations, e.g. U, C, S, etc. If this form contains classified information, stamp classification level on the top and bottom of this page.

17. LIMITATION OF ABSTRACT. This block must be completed to assign a distribution limitation to the abstract. Enter UU (Unclassified Unlimited) or SAR (Same as Report). An entry in this block is necessary if the abstract is to be limited.

Final Performance Report

Project Title: Local Electric Field Effects on Rhodium-Porphyrin and NHC-Gold Catalysts

Principal Investigator: Matthew W. Kanan

Project Publications:

1. "An Electric Field-Induced Change in the Selectivity of a Metal Oxide-Catalyzed Epoxide Rearrangement" Gorin, C. F.; Beh, E. S.; Kanan, M. W. *J. Am. Chem. Soc.* **2012**, *134*, 186-189.
2. "Interfacial Electric Field Effects on a Carbene Reaction Catalyzed by Rh Porphyrins" Gorin, C. F.; Beh, E. S.; Bui, Q. M.; Dick, G. R.; Kanan, M. W. *J. Am. Chem. Soc.* **2013**, *135*, 11257-11265.
3. "Electrostatic control of regioselectivity via ion pairing in a Au(I)-catalyzed rearrangement" Lau, V. M.; Gorin, C. F.; Kanan, M. W. *Chem. Sci.* **2014**, *5*, 4975-4979.
4. "Catalysis controlled by interfacial electric fields" Kanan, M. W.; Beh, E. S.; Gorin, C. F. US Patent application 14/240723.
5. "Local Electrostatic Effects on the Selectivity of Catalytic Reactions" Gorin, C. F. Stanford University Ph.D. Thesis, July 2014.

Executive Summary:

Controlling the selectivity of catalytic reactions is one of the greatest challenges of synthesizing organic compounds that are essential for health, technology, and defense. Chemists have traditionally addressed this problem using molecular design—i.e. controlling selectivity by changing the molecular structure of the reactants, catalysts or other reaction components. The overall goal of this project was to explore the possibility of using externally applied electric fields to control selectivity. The central idea is that a local electric field will change the potential energy surface for a reaction by creating field-dipole interactions with the reacting species and surrounding solvent molecules. This concept is appealing because all unique ground states and transition states that lead to specific reaction products have unique charge distributions that would respond differently to an electric field. The specific objective of this project was to investigate the effect of local electric fields on catalytic reactions at electrode-electrolyte interfaces. Applying a potential to an electrode in an electrolyte solution places charge density on the electrode that is balanced by the accumulation of electrolyte ions at the interface. The combination of these two charge densities creates large electric fields that on average are oriented normal to the surface. By confining catalytic reactions to this interfacial region, the effect of this electrostatic environment on the selectivity of the reaction can be studied. The major results of this project, including all the data and experimental procedures, are freely available in the publications listed above. The results are briefly summarized below.

To study electrostatic effects on catalytic reactions, a novel reaction vessel called the "parallel plate cell" was designed and fabricated. The cell is composed of two highly doped Si electrodes that sandwich a thin perfluorinated gasket with a small volume for the reaction solution. Each Si electrode is coated with an ultrathin (40–50 Å) layer of an insulating oxide such as Al₂O₃. With an electrolyte solution in between the two oxide-coated Si electrodes, application of a voltage across the electrodes creates electrochemical double layers at the oxide-electrolyte interfaces. The charge density at the interfaces is determined by the interfacial capacitances and the magnitude of the applied voltage. The oxide layers prevent Faradaic processes from occurring within the voltage limits before dielectric breakdown occurs. In the first reactions studied with this cell, the insulating Al₂O₃ layers were themselves used as catalysts for an epoxide rearrangement reaction. The reaction of *cis*-stilbene oxide with an Al₂O₃ surface results in formation of a mixture of aldehyde and ketone products. In the absence of a voltage, the reaction of *cis*-stilbene oxide with an Al₂O₃ layer in the parallel plate cell in an organic electrolyte solution gave the same ratio as was obtained with Al₂O₃ powder in a conventional flask reaction. The

aldehyde:ketone product ratio increased upon application of a voltage to the parallel plate cell. The magnitude of the change in the ratio increased as the voltage was increased, up to a 63-fold change at the maximum voltage that could be applied before dielectric breakdown. Various control experiments indicated that the change in product ratio depended on the charge density at the Al_2O_3 -electrolyte interfaces, which is consistent with an electrostatic effect on the reaction. Interestingly, the aldehyde:ketone ratio increased for both a positive and negative voltage drop at the Al_2O_3 -electrolyte interface. This result suggests that there may be significant dipole alignment of intermediates in the interfacial field or that the effect on selectivity arises from perturbation of the solvation properties in the interfacial region. Full details of this study are available in the publication (*J. Am. Chem. Soc.* **2012**, *134*, 186-189).

The next question addressed was whether an interfacial electric field could affect the selectivity of a reaction catalyzed by a molecular catalyst. An intramolecular carbene reaction catalyzed by a Rh porphyrin was selected as a model reaction for this study. A diazoketone substrate was designed to react with Rh porphyrin catalysts via a Rh metallocarbenoid intermediate to form a mixture of intramolecular cyclopropanation and C–H insertion products. Under traditional homogeneous reaction conditions, the reaction favors cyclopropanation over insertion by a ratio of approximately 10:1. When the Rh porphyrin was localized to the oxide–electrolyte interface in the parallel plate cell, application of a voltage to the cell changed the product ratio in a direction that depended on the oxide surface chemistry. The Rh porphyrin was localized to the interface by covalent attachment through phosphonate linkages or spontaneous physisorption under the experimental conditions. With an Al_2O_3 oxide or any insulating oxide coated with an alkyl phosphonate monolayer, application of a voltage caused the cyclopropanation:insertion product ratio to decrease. The magnitude of the decrease was dependent on the charge density at the interface and the maximum effect observed was to change the ratio to 1:2 in favor of the insertion product at the most highly charged interface. This effect was attributed to an electrostatic perturbation of the potential energy surface for the reaction. With a TiO_2 oxide coating, however, increasing the charge density at the interface caused the cyclopropanation:insertion product to increase. At the highest charge density that could be achieved before dielectric breakdown, the ratio was >100:1. It was determined through a variety of additional experiments that a charge density–induced chemical interaction between the TiO_2 surface and the Rh porphyrin catalyst was responsible for the selectivity change. Full details of this study are available in the publication (*J. Am. Chem. Soc.* **2013**, *135*, 11257–11265).

The experiments in the parallel plate cell showed that polarized electrode–electrolyte interfaces could significantly change the selectivity of catalytic reactions. Elucidating the specific electrostatic or other interactions that are responsible for the selectivity changes is challenging because the interfacial environment is highly complex and the energetic differences associated with the observed selectivity changes are small. To study electrostatic effects in a simpler context, we studied the effects of ion pairing on the selectivity of an intramolecular rearrangement catalyzed by cationic Au(I) complexes. The reaction selected was the rearrangement of aryl alkynyl sulfoxides to form dihydrobenzothiepinones via a putative Au metallocarbenoid intermediate. With aryl alkynyl sulfoxides that are substituted at the 3 position, the reaction yields two regioisomeric products. The regioselectivity is very difficult to control because it is not very sensitive to the ligand on the Au(I) complex. The reaction was performed with a variety of cationic Au(I) catalysts with different counterions in solvents that spanned a range of dielectric constants (ϵ). Using diffusion NMR techniques, it was determined that the Au(I) catalysts are tightly ion paired to their counterions in solvents with $\epsilon < 5$ and essentially non-paired in solvents with $\epsilon > 6$. For solvents in which there is no ion pairing, the regioselectivity of the reaction (i.e. the product ratio) was insensitive to ϵ . For solvents in with $\epsilon < 5$, however, the ratio changed monotonically as ϵ was decreased. The magnitude of the selectivity change depended on the

identity of the substituent at the 3 position. The largest change (6.3-fold from reaction in solvents with $\epsilon > 6$ to reaction in toluene, for which $\epsilon = 2.2$) was obtained with a CF_3 substituent, and, at the other extreme, almost no change was observed with a CH_3 substituent. To understand this disparity, DFT calculations were performed for the two putative product-determining transition states for each substrate. It was observed that the magnitude of the change in the product ratio in going from high- ϵ to low- ϵ solvent was correlated with the magnitude of the difference in dipole moments between the two competing transition states. In all cases, ion pairing favored the product resulting from the more polar transition state. It was concluded that ion pairing electrostatically differentiates the competing transition states by a field-dipole effect. Full details of this study can be found in the publication (*Chem. Sci.* **2014**, *5*, 4975–4979).

In summary, the project has demonstrated the feasibility of two methods for exploiting electrostatic effects to change the selectivity of reactions: using electrically polarized solid-liquid interfaces and using ion pairs in low- ϵ solvents. Ongoing work is exploring the use of electrostatic effects derived from ion pairing to control the selectivity of synthetically important group transfer reactions and the use of ferroelectric materials as dispersible, permanently polarized interfaces that substitute for electrode-electrolyte interfaces.

1.

1. Report Type

Final Report

Primary Contact E-mail

Contact email if there is a problem with the report.

mkanan@stanford.edu

Primary Contact Phone Number

Contact phone number if there is a problem with the report

650-725-3451

Organization / Institution name

Stanford University

Grant/Contract Title

The full title of the funded effort.

(NII)-Local Electric Field Effects on Rhodium-Porphyrin and NHC-Gold Catalysts

Grant/Contract Number

AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".

FA9550-11-1-0293

Principal Investigator Name

The full name of the principal investigator on the grant or contract.

Matthew W. Kanan

Program Manager

The AFOSR Program Manager currently assigned to the award

Michael Berman

Reporting Period Start Date

09/30/11

Reporting Period End Date

09/30/14

Abstract

Controlling the selectivity of catalytic reactions is one of the greatest challenges of synthesizing organic compounds that are essential for health, technology, and defense. The purpose of this project was to investigate the use of externally applied electric fields to control the selectivity of reactions in a way that is complementary to conventional methods. Using a custom reaction vessel, it was shown that the selectivity of reactions that are confined to an insulating electrode–electrolyte interface could be altered by the application of a voltage across the interface. The magnitude of the selectivity changes depended on the charge density that accumulated at the interface, which was controlled by the voltage and the interfacial capacitance. The selectivity of an Al₂O₃-catalyzed epoxide rearrangement reaction was changed by up to a factor of 63 at the highest charge density that could be achieved before dielectric breakdown. The selectivity of a Rh porphyrin–catalyzed intramolecular carbene reaction could be altered by a total of a factor of 200 depending on the charge density and the surface chemistry of the electrode–electrolyte interface. It was proposed that the charge density affects the reaction outcome through local field–dipole interactions with the reacting species

themselves and/or the surrounding solvent molecules. In a separate set of experiments, it was shown that field–dipole interactions that arise in tight ion pairs could be exploited to control selectivity. The counterion to a reactive complex in a tight ion pair preferentially stabilizes transition states with the largest dipole moments. These effects were demonstrated for a alkynyl sulfoxide rearrangement reaction catalyzed by cationic Au(I) complexes.

Distribution Statement

This is block 12 on the SF298 form.

Distribution A - Approved for Public Release

Explanation for Distribution Statement

If this is not approved for public release, please provide a short explanation. E.g., contains proprietary information.

SF298 Form

Please attach your [SF298](#) form. A blank SF298 can be found [here](#). Please do not password protect or secure the PDF. The maximum file size for an SF298 is 50MB.

[AFD-070820-035_Kanan.pdf](#)

Upload the Report Document. File must be a PDF. Please do not password protect or secure the PDF. The maximum file size for the Report Document is 50MB.

[Final Performance Report-AFOSR.pdf](#)

Upload a Report Document, if any. The maximum file size for the Report Document is 50MB.

Archival Publications (published) during reporting period:

Changes in research objectives (if any):

Change in AFOSR Program Manager, if any:

Extensions granted or milestones slipped, if any:

AFOSR LRIR Number

LRIR Title

Reporting Period

Laboratory Task Manager

Program Officer

Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, \$K)

	Starting FY	FY+1	FY+2
Salary			
Equipment/Facilities			
Supplies			
Total			

Report Document

Report Document - Text Analysis

Report Document - Text Analysis

Appendix Documents

2. Thank You

E-mail user

Dec 31, 2014 17:25:16 Success: Email Sent to: mkanan@stanford.edu